
(12) UK Patent Application (19) GB (11) 2 112 789 A

(21) Application No 8234971
(22) Date of filing 8 Dec 1982
(30) Priority data
(31) 8124379
(32) 29 Dec 1981
(33) France (FR)
(43) Application published
27 Jul 1983
(51) INT CL³
C08L 23/02 77/12
(52) Domestic classification
C3M 106 119 139 140 202
XC
U1S 1384 1425 3032 3042
C3M
(56) Documents cited
GB 1055175
(58) Field of search
C3M
C3V
(71) Applicants
Ato Chimie,
(France),
12/16 Allee des Vosges,
92400 Courbevoie,
France.
(72) Inventors
Gerard Deleens
(74) Agent and/or Address for
Service
Withers and Rogers,
4, Dyer's Buildings,
Holborn,
London EC1N 2JT.

(54) New polyolefins based
compositions

(57) The present invention concerns a new composition formed of an intimate mixture of 1 to 99% of one or several polyolefins and of 99 to 1% of one or several polyetheresteramides. Such compositions provide worked objects having a high shock resistance and improved antistatic properties.

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SPECIFICATION

New polyolefins based compositions

5 The present invention concerns new compositions based on polyolefins and also concerns particular applications of these compositions. 5

The polyolefins (polyethylene, polypropylene, etc.) are advantageously used in a large number of applications. It is known, however, that these polyolefins are not entirely satisfactory for certain applications demanding shock-resistance properties, dyeing affinity, aptitude to be painted or antistatic properties, for 10 example.

Therefore, for many years, it has been sought to improve the shock-resistance properties of the products obtained by moulding, extrusion or injection of the polyolefins, such tubes, or materials destined to be used in the automobile, electrical etc. construction industries. Attempts have also been made to improve their dyeing affinity and their aptitude to be painted, in order to give them certain colorations allowing the use of 15 these materials for construction and decoration. Furthermore, for many years it has been sought to dye certain polyolefins such as polyolefins that have not been satisfactorily dyed until now. 15

The present invention enables the above-mentioned drawbacks to be overcome. Undeeds, it allows conferring on new products based on polyolefins shock-resistance properties, thus widening the range of use of the polyolefins. Furthermore, it enables obtention of products based on polyolefins having various 20 colorations and improved antistatic properties. 20

The present invention is based on the surprising and unexpected observation that the polyolefins are totally miscible with certain defined compounds and that the compositions formed of a mixture of polyolefins and of the said compounds have improved shock-resistance properties at low temperature and show improved dyeing affinity and antistatism. 25

The present invention concerns a composition formed of an intimate mixture of one or several polyolefins and one or more polyetheresteramides and containing possibly organic or mineral fillers, the said mixture being formed of 1 to 99% by weight polyolefin and 99 to 1% by weight polyetheramide. 25

By polyetheresteramide, is meant not only statistic polyetheresteramides (i.e. formed by random chaining of various monomer constituents) by also polyetheresteramide blocks, i.e. formed of blocks whose various 30 constituents have a certain chain length. 30

The polyetheresteramides are, as is known, the product of copolycondensation of polyamide blocks having reactive extremities with polyether blocks having reactive extremities, such as among others:

- polyamide blocks having dicarboxylic chain-ends with either α , ω -dihydroxyl polyoxyalkylene or polyetheriol blocks or polyetherdiamine blocks (by cyanoethylation and hydrogenation of the 35 polyetherdiol; 35

- polyamide blocks having diamino chain-ends with polyether blocks having carboxylic chain-ends. 35

Such products are described in French patents 74-18913 and 77-26678, the contents of which must be taken into account in the present description.

According to one embodiment of the invention, polyamide blocks of polyetheresteramides are preferably 40 formed of 6, 6.6, 6.12, 11 or 12 polyamide (PA-6, PA-11, PA-6.6, PA-6.12, PA-12) or copolyamides resulting from the polycondensation of their monomers. 40

Preferably, the molecular weight of these polyamide blocks is comprised between 500 and 10 000 and more especially between 1000 and 5000.

According to another embodiment of the invention, the polyether blocks, comprise polytetramethylene 45 glycol (PTMG), polypropylene glycol (PPG), or polyethylene glycol (PEG). 45

Preferably, the molecular weight of the polyethers is comprised between 150 and 6000 and more especially between 400 and 3000.

According to a further embodiment of the invention, the polyetheresteramide mentioned herein-above is formed from 5 to 85% and more especially from 30 to 80% polyether and 95 to 15% and preferably from 70 to 50 20% polyamide. 50

According to one form of realisation of the invention, the polyolefin consists of polypropylene (PP), Polyethylene (PE), their mixtures or copolymers or the ionomer resins sold under the denomination Surlyn® of DuPont of Nemours.

Preferably, the said mixture is formed of 70 to 97% polyolefin and 30 to 3% polyetheresteramide.

55 The organic or mineral loads that the said composition can contain comprise the standard loads such as silica, titanium oxide, talc, mica, kaolin, magnesium, glass fibers, carbon black, vermiculite, glass beads, calcium carbonate, carbon fibers, used in association with polymer compositions. 55

Of course, the said compositions can contain standard additives such as anti-UV, light and thermal stabilisers, stripping or demolding agents, etc.

60 The process for the obtention of these compositions consists in working with a mixture of the two raw materials in dry pulverulent or granular form and in treating the mixture obtained in single or double screw extruder or kneading apparatus such as Banbury® or Buss® or, further, in calendering apparatus such as screw rolling, etc. It is also possible to operate, by mechanical mixing, in the hopper of the extruder or injection presses prior to extrusion or injection. 60

65 The present invention also concerns applications of the said compositions, especially for the production of 65

shock-resistant and antistatic objects by moulding, extrusion, injection. It also concerns worked objects and especially tubes, films, casing, etc. obtained from these compositions and subsidiarily concerns coloured or painted worked products obtained from these compositions.

Other aims and advantages of the present invention will become apparent by reading through the following description and examples which are given by way of non-limitative illustration.

Examples 1 to 4

Operating takes place in a double screw Werner Pfleiderer extruder, having a screw rotation speed of 50 t/mn.

The flow-rate of the extruder is 20 kh/h. The temperature graph in the extruder is 225-230-240-230°C from the entry to the exit.

As polyolefin is used in these examples 3020 SN-3 grade homopolymer polypropylene manufactured and sold by the company ATO CHIMIE whole melting index (M.I.)=8 (determined at a temperature of 230°C under a load of 5 kg).

The polyetheresteramide used is formed from 30% PA-12 having a molecular weight of about 850 and 70% PTMG whose molecular weight is about 2000.

The polyolefin/polyetheresteramide ponderal ratios in the compositions according to Examples 1 to 4 are respectively 95/5, 90/10, 85/15 and 80/20.

The physical properties of the compositions obtained on test samples obtained from these compositions are determined and the results are listed in TABLE 1.

Example 5

The same polyolefin as that in Examples 1 to 4 is used, and while operating under the same conditions, is combined with a polyetheresteramide formed from 50% PA-12 having a molecular weight of 2000 and 50% PTMG having a molecular weight of 2000.

The polypropylene/polyetheresteramide ponderal ratio is 90/10.

The physical properties of the composition obtained, determined on test samples mounted from these compositions are listed in Table 1.

Examples 6 and 7

The same polyolefin as that in Examples 1 to 4 (3020 SN-3 grade polypropylene) is used while operating under the same conditions, and is combined with a polyetheresteramide formed from 60% PA-6 having a molecular weight of about 1300 and 32% PPG having a molecular weight of about 600.

The polypropylene/polyetheresteramide ponderal ratios are respectively 90/10 (Example 6) and 85/15 (Example 7).

The physical properties determined on the test samples obtained from these compositions are listed in Table 1.

Example 8

Operating conditions are identical to those described in Example 5, but the polyetheresteramide used is formed from 50% PA-6 having a molecular weight of about 1500 and 50% PEG having a molecular weight of about 1500.

The physical properties determined on the test samples obtained from these compositions are listed in Table 1.

Example 9

By way of test sample, operating is carried out under identical conditions to those described in Examples 1 to 4, without adding polyetheresteramide to the olefin used, this olefin consisting of the propylene homopolymer sold by the Company ATO CHIMIE under the reference 3020 SN-3. The physical properties determined on a test sample are listed in Table 1.

Example 10

Also by way of test sample, operating is carried out according to the same method described in Examples 1 to 4, without adding polyetheresteramide and using "hypershock" grade polypropylene sold by the Company ATO CHIME under reference 3-4- MNG.

Table 1 lists the results of determinations carried out on a test sample obtained from this composition according to Examples 1 to 10.

It is noted by analysis of these results, with an experimental margin of error, that:

Shore hardness of test samples obtained from compositions according to the invention is lower than the Shore hardness of the polypropylene homopolymer of Example 9 and equivalent, on average to that of the "hypershock" polypropylene copolymer of Example 10.

The VICAT temperature, of the test samples formed from compositions according to the invention is generally comprised between the VICAT temperature of the "Hyper shock" copolymer of Example 10 and the VICAT temperature of the homocopolymer of Example 9.

The moduli of bending of the test samples of the compositions according to Examples 1 to 8 are

comprised between those of the test samples of the "hyper shock" copolymer of Example 10 and the homopolymer of Example 9.

• The densities are higher for the compositions according to Examples 1 to 8, than those of the densities of samples 9 and 10.

5 • Shock-resistance at 23°C and 0°C of the samples of Examples 1 to 8 is clearly higher than that of the test samples of Example 9 and in most of those of Example 10. 5

Furthermore, the antistatic measures were carried out on obtained moulded masses formed from compositions according to Examples 1 to 10. The appreciation test of antistatic power consists in developing by friction electrostatic charges, always in identical conditions, and appreciating the current thus produced

10 by the cigarette ash test. 10

It is observed, with an experimental margin of error, that the products of Examples 1 to 8 present antistatic properties which are clearly higher than those of the products of Examples 9 and 10.

Furthermore, compositions of Examples 1 to 10 were used to manufacture housings for radio receiver sets. These receiver sets are plunged into a hydroacetic solution at 80°C contained in a dyeing vat. This

15 hydroacetic solution has the following composition: 15

- AJL dimacid blue 3%
- Sunaptol LT 0.1%
- Acetic acid at 80% up to pH 5.

20 20

After one hour's immersion, the housings are removed from the said vat and rinsed.

TABLE I

EXAMPLE	1	2	3	4	5	6	7	8	9	10
Melt index	5	5.5	6	6.4	5	4	4	5	5	4
Density	0.910	0.915	0.920	0.925	0.915	0.925	0.930	0.925	0.905	0.895
Moduli of bending	13500	12700	12000	11700	13000	14000	13500	13000	15000	12500
IZOD Shock 23°C	20	60	N.C.*	N.C.*	40	15	20	35	4.5	50
0°C	10	17	20	N.C.*	13	8	10	12	2.5	15
Shore D hardness	63	61	60	58	63	65	63	63	70	61
VICAT temperature	147	144	142	140	148	151	150	150	152	143

* N.C. = does not break;.

It is observed that the housing obtained from the compositions according to Examples 9 and 10 are not dyed, and dyed not having "fixed" to the material of which they are formed. On the other hand, in the case of housing obtained from compositions of Examples 1 to 8, a dark blue coloration is obtained.

5 Examples 11 to 15

Operating takes place according to the same method as that used in Examples 1 to 4, the polyolefin consisting of LACQTENE® 1055 MN-20 (high pressure, low density polyethylene manufactured by the Company ATO CHIMIE) and polyetheresteramides such as indicated in TABLE II in which the ponderal ratio of PLACQTENE®/polyetheresteramide used is also shown.

10 The physical properties of the products obtained from these compositions are determined and it is noted that shock resistance, antistatism and dyeing affinity are clearly improved for the products obtained from compositions according to Examples 11 to 14 by comparison with LAQTENE® of Example 15.

TABLE II

EXAMPLE	11	12	13	14	15
· Polyetheresteramide					
20 - polyamide	PA-12	PA-12	PA-6	PA	-
· molecular weight	800	2850	4200	7900	-
25 - polyether	PTMG	PTMG	PPG	PPG	-
· molecular weight	1800	3000	4200	1600	-
- polyamide/polyether	30/70	40/60	68/32	50/50	-
30 · lacqtene/ polyetheresteramide	95/5	90/10	90/10	85/15	100/0

35 Examples 16 to 19

Mixtures identical to those of Examples 2, 9, 11 and 15 respectively are prepared, to which is added a load consisting (expressed in ponderal proportions) 30% glass fibers, having a length of about 1 mm.

The covers of the housing of the radio sets are manufactured from these mixtures. To these covers is applied by pulverisation a layer of industrial grey glycerophthalic lacquer. After drying, it is noted by use of the adhesive band test that the layer of paint adheres to the covers obtained from the compositions of Examples 16 and 18. On the contrary, the covers obtained from compositions of Examples 17 and 19 (formed respectively from pure polypropylene (of Example 9) and pure polyethylene (of Example 15) loaded with glass fibers), do not give rise to "fixing" of the paint layer.

Of course, the present invention is in no way limited to the embodiments of the invention described and shown herein-above and can be adapted to numerous variations available to the man skilled in the art, according to the applications envisaged and without departing from the spirit of the invention.

Herein-above, for convenience' sake, the usual commercial names of polytetramethylene glycol, polyethylene glycol and polypropylene glycol have been used which correspond according to the official nomenclature to polyoxytetramethylene glycol, polyoxyethylene glycol and polyoxypropylene glycol.

CLAIMS

1. A new composition formed from an intimate mixture of one or several polyolefins and from one or several polyetheresteramides, the said mixture being formed from 1 to 99% by weight polyolefin and 99% to 1% by weight polyetheresteramide.

2. A composition according to Claim 1, wherein the polyetheresteramides are statistic polyetheresteramides.

3. A composition according to Claim 1, wherein the polyetheresteramides consist of products of the copoly-condensation of block polyamides having reactive ends with polyether blocks having reactive ends, such as among others:

· polyamide blocks having dicarboxylic chain-ends with either polyetherdiol blocks or polyetherdiamine blocks (by cyanoethylation and hydrogenation of the polyetherdiol;

· polyamide blocks having diamino chain-ends with polyether blocks having carboxylic chain-ends..

4. A composition according to any one of Claims 1 to 3, wherein the polyamide blocks of the polyetheresteramides are formed preferably from 6, 11, 6.6, 6.12 or 12 polyamide (PA-6, PA-11, PA-6.6,

PA-6.12, PA-12) or copolyamide resulting from the copolycondensation of their monomers.

5. A composition according to Claim 4, wherein the molecular weight of these polyamide blocks is comprised between 500 and 10,000 and more particularly between 1,000 and 5,000.

6. Composition according to any one of Claims 1 to 3, wherein the polyether blocks consist of
5 polyoxytetramethylene glycol (PTMG), polyoxypropylene glycol (PPG) or polyoxyethylene glycol (PEG).

7. Composition according to Claim 6, wherein the molecular weight of the polyethers is comprised between 150 and 6,000 and more particularly between 400 and 3,000.

8. Composition according to any one of Claims 1 to 7, wherein the said polyetheresteramide is formed from 5 to 85% and more particularly from 30 to 80% polyether and 95 to 15% and preferably from 70 to 20%
10 polyamide.

9. Composition according to any one of Claims 1 to 8, wherein the polyolefin consists of polypropylene (PP), polyethylene (PE), their mixtures or copolymers, or of ionomer resins sold under the denomination of SURLYN® of the Company DuPont of Nemours.

10. Composition according to any one of Claims 1 to 9, wherein the said mixture is formed from 70 to
15 97% polyolefin and from 30 to 3% polyetheresteramide.

11. Composition according to any one of claims 1 to 9, wherein it contains an organic or mineral load consisting of loads such as silica, titanium oxide, talc, mica, kaolin, magnesite, glass fibres, carbon black, vermiculite, glass beads, calcium carbonate, calcium fibres, and possibly additives such as anti-UV, heat or light stabilizers, demolding agents.

20 12. Application of compositions according to any one of claims 1 to 10, to the obtention of worked objects presenting a higher shock-resistance and improved anti-static properties.

13. Worked objects and others obtained from the composition according to any one of claims 1 to 10, presenting a high shock resistance and improved anti-static properties.

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- 1/1 - (C) WPI / DERWENT
AN - 92-188650 c30!
AP - JP900245064 900914
PR - JP900245064 900914
TI - Polypropylene film with paper-like appearance and hydrophilic nature - comprises crystalline polypropylene, thermoplastic resin incompatible with polypropylene, polyesterether amide and modified olefin polymer
IW - POLYPROPYLENE FILM PAPER APPEAR HYDROPHILIC NATURE COMPRISE CRYSTAL POLYPROPYLENE THERMOPLASTIC RESIN INCOMPATIBLE POLYPROPYLENE POLYESTERETHER AMIDE MODIFIED POLYOLEFIN POLYMER
PA - (TORA) TORAY IND INC
PN - JP4122736 A 920423 DW9223 C08J5/18 007pp
ORD - 1992-04-23
IC - B29C55/12 ; B29K23:00 ; B29L7:00 ; B32B27/32 ; C08J5/18 ; C08L23/10 ; C08L23:10 ; C08L23:14 ; C08L77/00
FS - CPI;GMPI
DC - A17 A23 A94 P73
AB - J04122736 A polyolefin film consists of 89-40 wt.% of a crystalline polypropylene (A), 5-30 wt.% of a thermoplastic resin (B) which has a heat distortion temp. of higher than 85 deg.C and is incompatible with the crystalline polypropylene, 5-20 wt.% of a polyetherester amide (C) and 1-10 wt.% of a carboxyl gp.-contg. modified olefin polymer (D), and has a wet tension of more than 55 dyne/cm.
- (B) is e.g. poly-4-methylpentene-1 (PMP) which has a m.pt. of higher than 230 deg.C and a Mw/Mn of less than 6. The crystalline polypropylene pref. contains a beta-crystal nucleating agent. Pref. at least one side of the polyolefin film is laminated to give a composite film.
- (A) is e.g. a propylene homopolymer or a propylene-ethylene copolymer with an ethylene content of less than 2 mol.%. The beta-crystal nucleating agent is e.g. quinacridone or quinacridone quinone. (C) is a copolymer composed of a polyamide component and a polyetherester component. The polyamide component is e.g. a polyamide prepd. by the ring opening polymerisation of epsilon-caprolactam. The polyetherester component is composed of a polyether part contg. e.g. polyethylene glycol and a polyester part contg. e.g. terephthalic acid. (D) is e.g. ethylene-methylmethacrylate copolymer.
ADVANTAGE - The polyolefin film has a paper-like appearance and a hydrophilic nature. It has high resistance to the lamellar stripping of its surface.
(0/0 to 32)

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